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MINERALOGICAL EXAMINATION OF TREATED ZINC OXIDE FUME LEACH RESIDUES

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MINERALOGICAL EXAMINATION OF TREATED ZINC OXIDE FUME LEACH RESIDUES

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ABSTRACT

Mineralogical examination of (1) a head sample of zinc oxide fume leach residue, (2) the product formed from a two-stage acid leach of the head material, and (3) two resulting flotation tails, shows that all consist predominantly of anglesite, $PbSO_4$. The head sample also contains abundant zinc-bearing oxide and a jarosite-like phase, but the latter was effectively removed by the two-stage acid leach. Sphalerite, which is present in all samples but is most abundant in the two tails, is interpreted to be the main source of the zinc values in the acid-leached samples.

Keywords: zinc oxide, fume leach residues, anglesite, jarosite, spinel, sphalerite, copper sulphide

ÉTUDE MINÉRALOGIQUE DES RÉSIDUS D'OXYDE DE ZINC TRAITÉS PAR LIXIVIATION FUMANTE

par

J.L. Jambor et D.R. Owens

RÉSUMÉ

Les résultats de l'étude minéralogique de (1) un échantillon de tête de résidus d'oxyde de zinc de lixiviation fumante, (2) du produit formé par lixiviation à l'acide en 2 étapes du matériel de tête, et (3) deux queues de flottation, démontrent qu'ils sont tous principalement composé d'anglésite, $PbSO_4$. L'échantillon de tête contient aussi une grande teneur en oxyde de zinc ainsi qu'une phase de jarosite, cette dernière est enlevée efficacement au cours de la lixiviation à l'acide en deux phases. La sphalérite présente dans tous les échantillons et surtout en abondance dans les deux queues, est la principale source des teneurs en zinc dans les échantillons traités par la lixiviation à l'acide.

Mots-clés: oxyde de zinc, résidus de lixiviation fumante, anglésite, jarosite, spinelle, sphalérite, sulfure de cuivre.

INTRODUCTION

Under the auspices of the Canada-Manitoba Mineral Development Agreement, Sherritt Gordon Mines Limited is carrying out an Oxide Residue Treatment Study for Hudson Bay Mining & Smelting Company Limited. The latter is considering processing its stockpile of zinc oxide fume leach residue to recover contained Cu, Pb, Zn, Ge, and precious metal values[1]. The initial testwork gave a zinc extraction lower than was anticipated, and thus oxidative acid pressure leaching was investigated as a potential method of removing copper sulphides that were recognized to be present and were thought to coat zinc oxide particles, thereby shielding the zinc oxide from liberation[1].

Subsequent testwork, however, showed that appreciable amounts of zinc remained in the residues. In March, 1987, four samples were submitted to W.J.S. Craigen with the request that these be examined mineralogically at CANMET.

MATERIALS

Four plastic bags containing fine-grained powders were received. Each was labelled according to the code number in Table 1. Compositional data were provided in an accompanying letter from G.L. Bolton, Manager, Process Research, Sherritt Gordon Mines Limited, who described the samples as follows:

(1) HEAD: zinc oxide fume leach residue as received from Hudson Bay Mining & Smelting Company.

(2) 1050-191: a two-stage leach residue of the HBM&S material produced by an acid leach at 150°C, followed by an acid leach at 100°C under SO_2 pressure.

(3) 1050-131-2FR: the flotation tails of a two-stage acid leach under SO_2 pressure.

(4) 1093-7-2: the flotation tails as for (3) above, but with low SO_2 pressure during the leaching stages.

For convenience, the above will be referred to as the head or (1) sample, and as samples (2), (3), and (4). The sandy-brown colour of the head sample contrasts with the neutral, light grey colour of the other three. The compositional data in Table 1 show that lead is the main constituent in all samples, that calcium may be moderately abundant in all samples, and that iron is a significant component only in the head sample. The zinc content of samples (2) to (4) is much lower than that of the head sample, but the nature of the zinc in the leach residues is the item of specific interest.

Table 1. Compositions of zinc oxide fume leach residues

Sample	Weight %							
	As	Cd	Ca	Cu	Fe	Pb	Si	Zn
Head	3.18	0.19	6.31	1.63	11.6	16.1	1.56	9.72
(2)	0.04	0.05	n.a.	0.34	0.43	35.4	n.a.	1.69
(3)	0.30	0.08	n.a.	0.75	0.40	30.1	2.43	2.77
(4)	0.70	0.07	9.51	1.20	0.98	27.8	3.19	2.72

PROCEDURES

A part of each of the as-received samples was mounted in polished sections which were prepared using non-aqueous media to minimize losses of possible water-soluble phases. Each of the powder samples also was

scanned using a Rigaku automated X-ray powder diffractometer equipped with a copper target, and each was recorded on a Guinier-deWolff X-ray diffraction pattern taken with cobalt radiation.

The polished sections were studied microscopically, and selected areas were examined by scanning electron microscopy and qualitative energy dispersive X-ray analysis. Several larger grains were extricated from the polished sections to obtain Debbye-Scherrer X-ray patterns using cameras of 57.3 mm diameter, and cobalt radiation.

Following the preliminary study of the samples, a portion of each of the as-received powders was leached twice with 1-litre portions of 20% ammonium acetate solution at 25°C. This process selectively leaches $PbSO_4$. The products were then filtered, water-washed, and dried at room temperature. Subsequently, a new set of polished sections was prepared, and the leached samples also were examined by X-ray powder-diffraction patterns and SEM-EDX techniques as outlined above. As well, the main copper sulphide in the samples was quantitatively analyzed by microprobe using wavelength spectrometry.

RESULTS

All of the as-received samples are rich in lead (Table 1), a large part of which is present as anglesite, $PbSO_4$. The abundance of this phase and the numerous diffraction lines in its X-ray powder pattern effectively mask the diffraction lines of other compounds in the samples. Nevertheless, other compounds identifiable in the X-ray patterns of the head sample are gypsum ($CaSO_4.2H_2O$), anhydrite ($CaSO_4$), sphalerite, and an abundant unidentified constituent whose X-ray pattern is similar to that of plumbojarosite-

jarosite. The identity of this major phase requires confirmation, but for convenience the substance is referred to as jarosite-like. Optical examination of the head sample confirmed the presence of numerous grains of sphalerite, and showed that small amounts of a blue, covellite-like copper sulphide are disseminated throughout the section. Traces of pyrite, a white (in reflected light) copper sulphide, and a pinkish copper-zinc sulphide were noted and qualitatively examined by SEM-EDX, but these phases are of no quantitative significance. Although some of the much more abundant blue copper sulphide occurs in sphalerite grains, or at their rims, the two minerals predominantly occur independently rather than in intimate association. Much of the copper sulphide is present as minute, disseminated, anhedral grains rather than in the rim textures expected if this phase formed a coating on other particles, such as those of zinc oxide.

Samples (2), (3), and (4) are similar in that they consist largely of anglesite. The jarosite-like phase, noted as a major component of the head sample, is present in trace amounts only in sample (4). Anhydrite is detectable in the X-ray patterns of (2) and (3), and gypsum is a conspicuous phase in sample (4). Sphalerite is detectable in sample (2), but is more abundant in (3) and (4). Sulphur is evident in all three samples, but is most abundant in (3). Polished-section observations show that sphalerite still occurs as disseminated anhedral grains (Fig. 1), but the major change from the head sample is that the blue copper sulphide, which is sparse in (2), has conspicuous rim textures in samples (3) and (4). These rims have a pronounced concentration at the margins of grains of sulphur, and at the margins of voids (Fig. 2). The voids, some of which are occupied by polished-section epoxy, may have been originally filled, or partly filled, by sulphur that has been lost during the polishing process.

Acetate-leached samples

Ammonium acetate leaching to remove anglesite from the as-received samples was extremely effective: not even a trace of the lead sulphate was detected on Guinier-deWolff X-ray patterns of the leached products. The procedure therefore also was effective in concentrating the zinc-bearing phases of specific interest in this study.

The leached head sample consists predominantly of the jarosite-like phase. Figures 3, 4, and 5 show some of the additional phases present, and their mode of occurrence. The blue copper sulphide does not appear to be present in sufficient quantity to account for the analytical value of 1.6 wt % Cu in the as-received sample, thus suggesting that some of the copper may reside in the jarosite-like phase. SEM-EDX analyses indicate that zinc is present in many phases, including silicate; discrete zinc-bearing compounds that probably account for the bulk of the element are a Zn-Fe oxide, probably of the type $ZnFe_2O_4$, and minor amounts of low-iron sphalerite (probably about 1% Fe).

The X-ray patterns of acetate-leached samples (2) and (3) are similar. The jarosite-like phase is absent and the main components are sulphur, sphalerite, and traces of the spinel-type Fe or Zn-Fe oxides. As well, a few additional diffraction lines are in the X-ray patterns, and these lines probably arise from the blue copper sulphide and the traces of silicates in the samples. Leached sample (4) is similar to the above, with the notable exceptions that the jarosite-like phase is present in a small amount, but the spinel phase is at very low trace levels or is absent. Microscopic studies and qualitative SEM-EDX analyses indicate that the sphalerite in these samples contains negligible iron; this compositional feature, plus some of the textures (Fig. 6, 8), suggest strongly that the sphalerite is a newly crystallized phase rather than an unreacted relict from the head sample.

The number of sphalerite grains in samples (3) and (4) is much higher than in sample (2). The blue copper sulphide, as was noted in the samples not leached with acetate solution, occurs mainly as well-defined rims in an atoll texture (Fig. 9).

High-magnification optical microscopy with oil-immersion lenses was used to determine whether the blue copper sulphide was deposited as coatings on sphalerite or any other phase. These observations indicated that the rim, or atoll, texture of the copper sulphide is related to vugs and is not an overgrowth or coating phenomenon. Where the copper sulphide is in contact with sphalerite, the contact is casual in that a propensity toward rimming is not evident. Nevertheless, casual contacts between sphalerite and copper sulphide are numerous, especially for the smaller sphalerite grains.

Blue copper sulphide

The blue copper sulphide in the samples has been referred to in general terms rather than as a specific compound. Although the sulphide has the optical properties of covellite, unequivocal confirmation by X-ray powder diffraction could not be obtained; thus, the possibility remained that an unknown copper phase resembling covellite could have formed under the crystallization conditions used to treat the fume leach residues. To resolve the uncertainty, two areas of the copper sulphide in leached sample (4) were analyzed by microprobe wavelength spectrometry. The results total only about 96 wt %, but the atomic ratios of copper to sulphur are close to 1:1 and indicate that this phase almost certainly is covellite. An interesting aspect of the analyses is that all probed spots in both of the analyzed areas consistently indicated that the copper sulphide contains about 0.6 to 1.0 wt % Ag. As the other constituents of the acid-leached

residues are unlikely silver carriers, it is probable that most of the silver in these residues is present in the copper sulphide. Silver values were not included in the assay data for the residues (Table 1).

Zinc oxide distribution

Spinel-type compounds of the type XFe_2O_4 are conspicuous components of the head sample. SEM-EDX qualitative analyses indicate that X can be Fe, Zn, or both. The presence of such relict spinels in the acid-leach residues would have a significant affect on the zinc partitioning if the spinel is zinc-bearing. Although the Guinier X-ray pattern of the acetate-leached head sample shows the presence of abundant spinel, in samples (2) and (3) the diffraction lines at the appropriate d-values are weak; accordingly, ambiguities in identification arise because of overlapping diffraction contributions from other minor phases in these mixtures. On the basis of the X-ray data alone, it was interpreted that trace amounts of spinel are present in acetate-leached samples (2) and (3), but that the spinel is either at very low trace levels or is absent in sample (4).

As a check on the X-ray results and interpretation, a specific search for zinc-bearing phases in samples (2) and (4) was done by SEM-EDX analyses. In sample (2), zinc was found to be present in various phases such as Zn silicate, Fe-Al silicate, Al-Fe-Pb silicate, and a zinc-predominant Fe-Al oxide; a significantly higher proportion of the zinc, however, occurs as sphalerite. In sample (4), similar but fewer zinc-bearing phases are present, and again the highest proportion of zinc occurs as sphalerite.

CONCLUSIONS

1. The principal phases in the head sample are anglesite, a jarosite-like mineral, and zinc-bearing oxides in the spinel group, some of which have the composition $ZnFe_2O_4$. Small amounts of copper sulphide are present, but the sulphide does not occur as rims that would shield the oxides from further reaction.

2. The two-stage leach effectively removed the jarosite-like phase, but zinc remains as sphalerite and possibly in traces of spinel-type compounds in samples (2) and (3).

3. Sphalerite in the head sample contains small amounts of iron, but sphalerite in all products from the two-stage leach is almost pure ZnS. The texture of sphalerite suggests that redeposition of at least some of the grains occurred during the two-stage leach.

4. Contacts among copper sulphide, zinc sulphide, and zinc-bearing oxide are casual rather that showing an affinity toward rim textures. Nevertheless, partial contacts between sphalerite and copper sulphide are numerous and could significantly affect flotation processing.

5. Both sphalerite and copper sulphide are noticeably more abundant in the two tails (samples 3 and 4) than in the two-stage leach residue (sample 2).

6. Sphalerite, as almost pure ZnS, is interpreted to be the principal source of the higher-than-expected zinc values in the two-stage acid leach residues.

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REFERENCE

1. Sherritt Gordon Mines Limited (1986): Hudson Bay Mining and Smelting Co. Limited oxide residue treatment, progress report 2, November to December 1986.

FIGURE CAPTIONS

Fig. 1-4. All photographs are of polished sections and were taken with reflected light, in air, at the same magnification. Bar scale at the bottom right of Figure 4 represents 0.06 mm.

Fig. 1. As-received sample (3) showing high-relief sulphur grains (arrows) and light grey sphalerite (e.g., sp).

Fig. 2. Large grain of light grey sphalerite (sp) and narrow rings of blue copper sulphide (arrows) in as-received sample (4).

Fig. 3. Acetate-leached head sample. Grain a is an iron oxide phase containing a small amount of zinc; grain b is a spherule of zinc-free iron oxide; grain c is pyrite; grain d is an iron silicate. Arrow points to an irregular, U-shaped grain of sphalerite.

Fig. 4. Large grains of sphalerite (sp), the upper one of which has a detached, almost complete rim of Zn-Fe oxide. The lower sphalerite grain is rim-free. Arrow points to one of two elongate, thread-like trains of Zn-Fe oxide. Acetate-leached head sample.

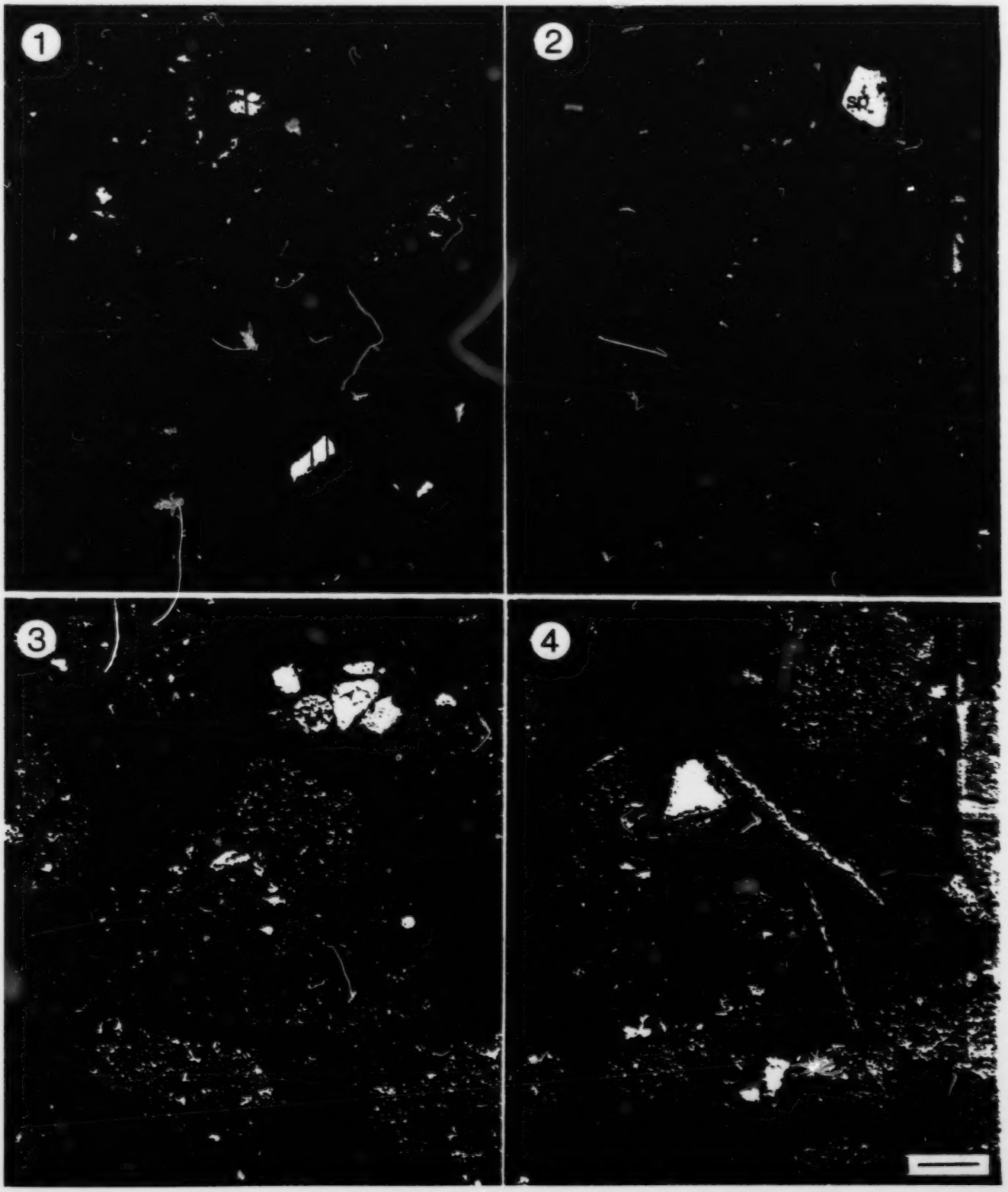
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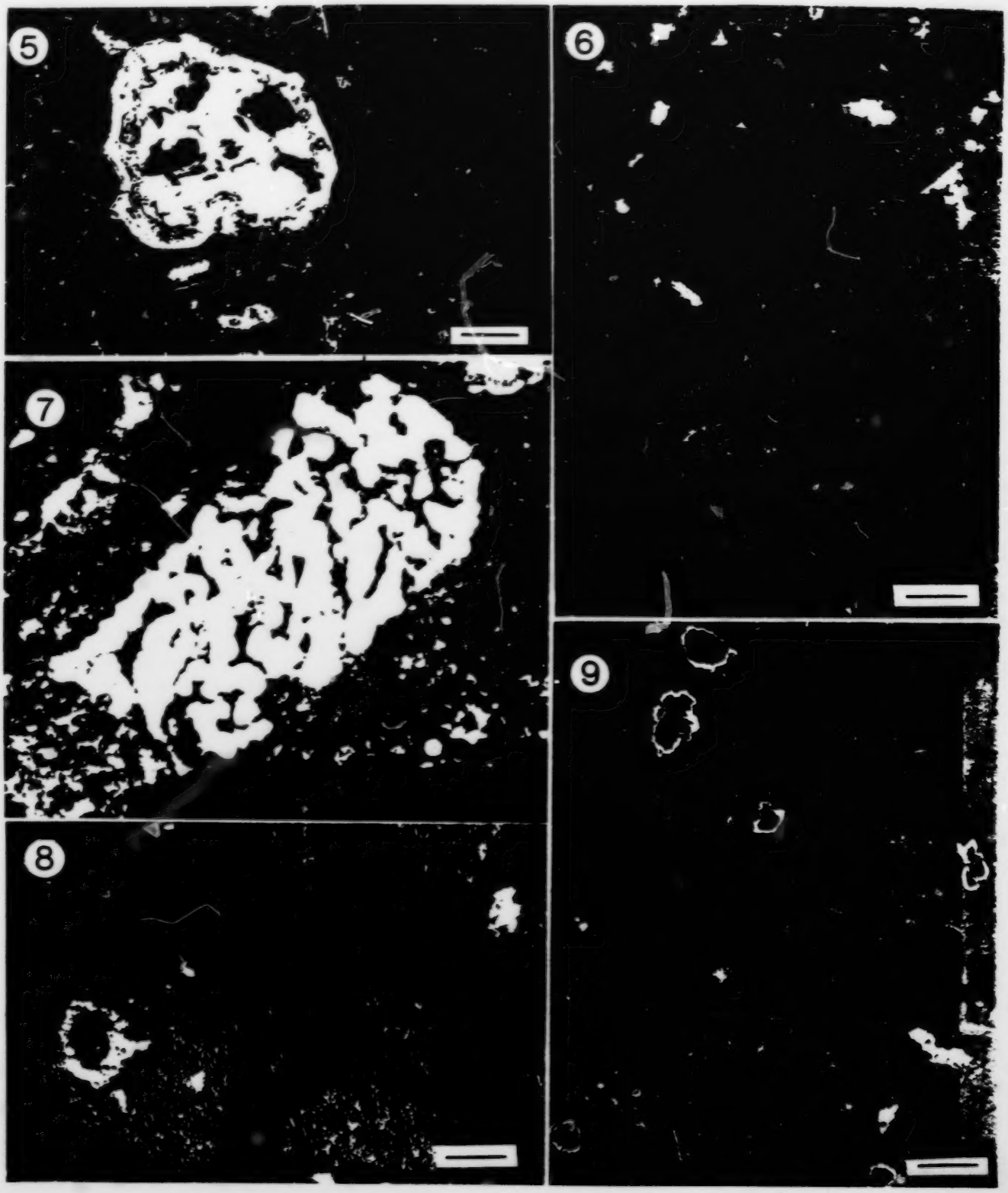
Fig. 5. Acetate-leached head sample showing a large grain of Fe oxide (medium grey with black pits) rimmed by a lighter grey phase that is another Fe oxide. Reflected light, air. Bar scale represents 0.03 mm.

Fig. 6. Reflected-light photo of acetate-leached sample (3) showing light grey sphalerite grains, with arrow at upper right pointing to a grain with irregular contacts suggestive of open-space crystallization. Arrow at bottom locates the dark grey aggregate of blue copper sulphide shown in Figure 7. Bar scale represents 0.06 mm.

Fig. 7. Backscattered electron image showing worm- and atoll-like aggregate of blue copper sulphide in acetate-leached sample (3).

Fig. 8. Reflected-light photograph of acetate-leached sample (3). Pits (black) have thin rims of copper sulphide. A well-defined ring of medium-grey sphalerite with an epoxy core is at the middle left. Bar scale represents 0.06 mm.

Fig. 9. Reflected-light photograph of acetate-leached sample (4) showing the typical ring-like form of the blue copper sulphide. Bar scale represents 0.06 mm.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